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Note

Reactions of cyclic anhydrides with aromatic primary amines: Part 2[†] — Synthesis of novel anilinic acids from a Diels-Alder adduct

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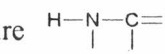
7-Oxabicyclo[2.2.1]hept-5-ene-2β, 3β-dicarboxylic acid anhydride **6** reacts with aromatic amines **7a-d** and **9** to furnish a series of 2-*N*-phenylcarbamoyl)-**8a**, 2-(*N*-tolylcarbamoyl)-**8b-d** and 2-(*N*-naphthylcarbamoyl)-7-oxabicyclo[2.2.1]hept-5-ene-3-carboxylic acids **10**. These amides show some insecticidal activity against adult insects of *Sitophilus spp* and compoud **10** is the most active in this series.

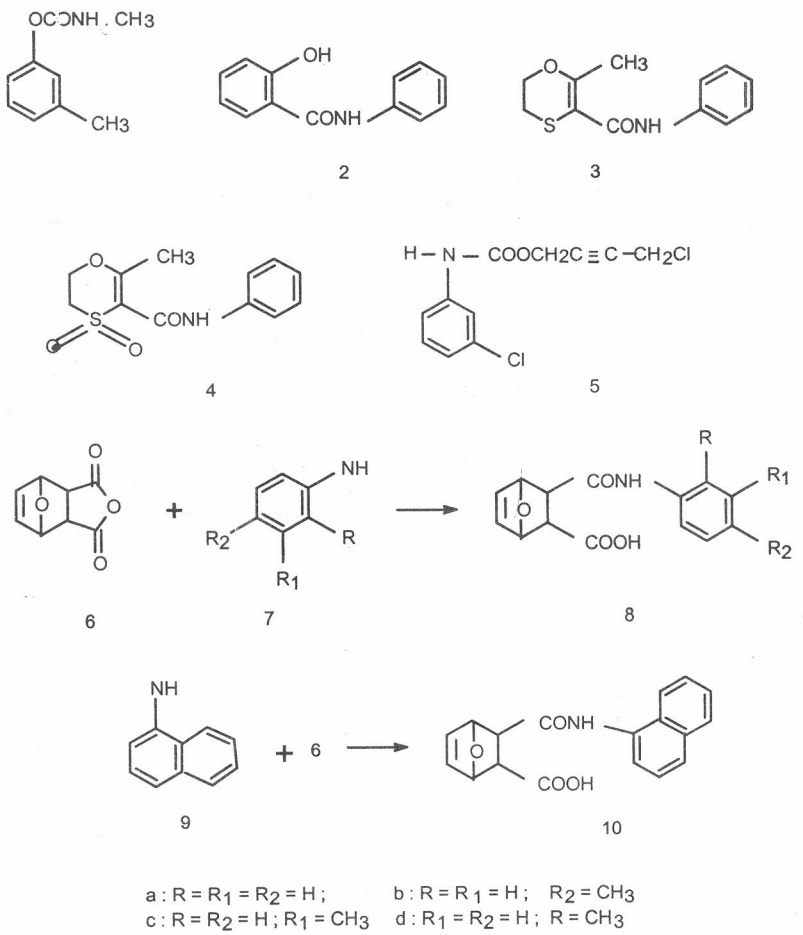
The fundamental linkage in pesticidal aryl and alkyl carbamates is probably the carbamoyl group. Many phenyl carbamates such as *m*-tolylmethyl carbamate **1** are insecticidal[1] while 2-hydroxyphenylanilide **2**, Carboxin **3** and Oxycarboxin **4** elicit fungicidal properpties[2,3]. Most herbicides that inhibit the photochemical oxidation of water have the common structural feature  where X is an atom with a lone pair of electrons (N or O)[3]. The carbamate herbicide barban **5** bears this group. In continuation of our search for new insecticides for biological screening and physico-chemical studies, we describe herein the synthesis of novel anilinic acids involving the reaction of a Diels-Alder adduct with aromatic amines.

The starting anhydride, *exo*-7-oxabicyclo[2.2.1] hept-5-ene-2β, 3β-dicarboxylic acid anhydride **6** was prepared as reported earlier[4]. Treatment of **6** with anilines **7a-d** and 1-naphthylamine **9**. in refluxing chloroform[5] gave the corresponding anilinic acids **8a-d** and **10** in good yields in a one-pot reaction. The IR of **8a** exhibited the carboxylic acid C=O absorption at 1720 and the amide C=O absorption at 1685 cm^{-1}. The bands at 3300 and 3115 cm^{-1} were characteristic of NH and OH functions respectively. The ^1H NMR of **8a** displayed a singlet at δ 10.60 which was assigned to OH of the carboxylic acid and a singlet at 2.38 due to methyl protons of the tolyl group. Replacement of the anhydride C=O absorption bands at 1860 and 1850 with the bands at 1710 and 1680 in **8b**, corresponding to the carboxylic acid and amide C=O bands respectively, suggested that the desired condensation had occurred. This was further supported by the effervescence given by **8a-d** and **10** with sodium bicarbonate solution indicating the presence of carboxylic group. These anilinic acids are of biological interest sicne the carboxyl group at C-3 in each compound, may be further converted into an amide function by treatment with amines. Integration in the aromatic region showed five aromatic protons for **8a**, four each for **8a-d** and seven for **10**. The downfield of the singlet at δ 8.7 is assignable to the NH proton of **7a** and this can be attributed to the anisotropic effect of the neighbouring carbonyl and phenyl groups.

The mass spectrum of **7a** showed peaks at m/z 259 (M^+), 242, 233, 215, 214, 191 which were consistent with the structure. The fragment at m/z 214 may be due to the loss of COOH from the molecular ion while m/z 233 peak is probably due to acetylene, and the peak at m/z 191 due to the loss of furan by a retro-Diels-Alder reaction. The common fragments m/z 273 and 272 for the isomeric compounds **8b-d** were obtained by the loss of a proton from the molecular ion to give the tropylium ion derivatives.

Biological Activity. Screening for insecticidal activity was carried out by topical application of compounds on maize grains as reported by Allotey[6]. Pirimiphos-methyl was used as a chemical standard[7] while neem leaves power served as a natural bioactive standard[8]. Results have been expressed as reported[9] earlier. Compounds **8a-d** and **10** were more active than neem leaves power *(Azadiricta indica)* but much less active than Pirimiphos-methyl, as protectants against maize weevils.

[†] For part 1, see, *Indian J Chem*, 37B, **1998**, 704.



Compound **10** was twice, **8a** about 1.4 times as active as, while **8c** was of comparable activity as *A. indica*. These compounds were more active than those reporter[9] earlier.

Experimental Section

General. All reagents were purified before use. Melting points were recorded on a Stuart melting point apparatus and are uncorrected. IR spectra were recorded in KBr dics or as nujol mull on a Perkin-Elmer 157G instrument (ν_{max} in cm^{-1}), ^1H NMR spectra in $CDCl_3$ on a Varian Associates A60 spectrophotometer using TMS as internal standard (chemical shifts in δ, ppm), and mass spectra on an AEI MS 902 instrument.

2-(*N*-Arylcarbamoyl)-7-oxabicyclo[2.2.1]hept-5-ene-3-carboxylic acids 8a-d: General procedure. A mixture of freshly distilled aromatic amines **7a-d** (0.05 mole) and 7-oxabicyclo[2.2.1]hept-5-eme-2β, 3β-dicarboxylic acid anhydride **6** (0.05 mole) in chloroform (100 mL) was heated under reflux for 3 hr[3]. The precipitate was left to cool for 2 hr, filtered and dried under suction. Recrystallisation from methanol furnished the anilinic acids **8a-d**. Their analytical and spectral data are given below:

Compound 8a. mp 149 °C yield 9.94g (77%). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.8; H, 5.0; N, 5.4. Found: C, 64.7; H, 5.0; N, 5.3%; IR (Nujol): 3300, 3115, 1720, 1685, 1080; ^1H NMR ($CDCl_3$): 10.60 (1H, s, COOH), 8.70 (1H, brs, CONH), 7.52 (5H, m, ArH), 6.62 (2H, m, H-5 and H-6), 5.44 (2H, m, H-1 and H-4), 3.44 (2H, m, H-2 and H-3); MS: m/z 259 (M^+), 242, 233, 215, 214, 191.

Compound 8b. mp 188 °C, yield 12.60g (92%). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.9; H, 5.5; N, 5.1. Found: C, 65.8; H, 5.6; N, 5.0%; IR (KBr): 3290, 3085, 1710, 1680, 1085; ^1H NMR ($CDCl_3$); 10.58

(1H, s, COOH), 8.6 (1H, brs (CONH), 6.90 - 7.15 (2H, d, ArH, J = 8.5 Hz), 7.35-7.50 (2H, d, J =8.5 Hz, ArH), 6.65 (2H, m, H-5 and H-6), 5.45 (2H, m, H-1 and H-4), 3.45 (2H, m, H-2 and H-3), 2.38 (3H, s, $ArCH_3$); MS: m/z 273 (M^+), 272, 256, 249, 228, 205.

Compound 8c.mp 120 °C, yield 12.3g (90%). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.9; H, 5.5; N, 5.1. Found: C, 65.8; H, 5.5; N, 5.2%; IR (KBr): 3280, 3090, 1695, 1675, 1080; ^1H NMR ($CDCl_3$): 10.62 (1H, s, COOH), 8.65 (1H, brs, CONH), 7.42 (4H, m, ArH), 6.64 (2H, m, H-5 and H-6, vinyl), 5.46 (2H, m, H-1 and H-4, allylic), 3.44 (2H, m, H-2 and H-3), 2.36 (3H, s, $ArCH_3$); MS: m/z 273 (M^+), 272 (M^+-1).

Compound 8d. mp 124 °C, yield 12.8g (94%). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.9; H, 55.5; N, 5.1. Found: C, 65.7; H, 5.5; N, 5.0%; IR (KBr): 3275, 3080,. 1690, 1085; ^1H NMR ($CDCl_3$): 10.64 (1H, s, COOH), 8.60 (1H, brs, CONH), 7.35 (4H, m, ArH), 6.662 (2H, m, H-5 and H-6, vinyl), 5.45 (2H, m, H-1 and H-4, allylic), 3.45 (2H, m, H-2 and H-3), 2.38 (3H, s, $ArCH_3$); MS; m/z 273 (M^+), 272, 228, 205.

2 -*N*- (1-Naphthylcarbamoyl)- 7- oxabicyclo-[2.2.1]hept-5-ene-3-carboxylic acid 10. A suspension of 1-naphthylamine (15.5g, 0.05 mole) and 7-oxabicyclo[2.2.1]hept-5-ene-2β, 3β-dicarboxylic acid anhydride (8.3g, 0.05 mole) in chloroform (150 mL) was refluxed for 3 hr. The precipitate was left overnight, filtered, dried under suction and recrystallised from methanol to give brown crystals of **10**, yield 10.2g (61%), mp 150 °C. Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.9; H, 4.9; N, 4.5. Found: C, 69.8; H, 4.9; N, 4.6%: IR (KBr): 3400, 3010, 1710, 1680, 1080; ^1H NMR ($CDCl_3$): 10.65 (1H, s, COOH), 8.72 (1H, brs, CONH), 7.65 (7H, m, ArH), 6.60 (2G, m, H-5 and H-6), 5.40 (2H, m, H-1 and H-4), 3.42 (2H, m, H-2 and H-3); MS: m/z 309 (M^+), 292, 265, 264, 241.

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